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Polar tropospheric ozone depletion events observed in the International Geophysical Year of 1958

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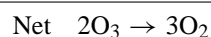
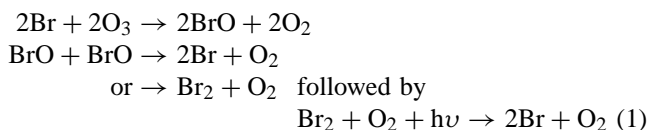
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Abstract. The Royal Society expedition to Antarctica established a base at Halley Bay, in support of the International Geophysical Year of 1957–1958. Surface ozone was measured during 1958 only, using a prototype Brewer-Mast sonde. The envelope of maximum ozone was an annual cycle from 10 ppbv in January to 22 ppbv in August. These values are 35% less at the start of the year and 15% less at the end than modern values from Neumayer, also a coastal site. This may reflect a general increase in surface ozone since 1958 and differences in summer at the less windy site of Halley, or it may reflect ozone loss on the inlet together with long-term conditioning. There were short periods in September when ozone values decreased rapidly to near-zero, and some in August when ozone values were rapidly halved. Such ozone-loss episodes, catalysed by bromine compounds, became well-known in the Arctic in the 1980s, and were observed more recently in the Antarctic. In 1958, very small ozone values were recorded for a week in midwinter during clear weather with light winds. The absence of similar mid-winter reductions at Neumayer, or at Halley in the few measurements during 1987, means we must remain suspicious of these small values, but we can find no obvious reason to discount them. The dark reaction of ozone and seawater ice observed in the laboratory may be fast enough to explain them if the salinity and surface area of the ice is sufficiently amplified by frost flowers.

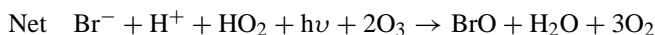
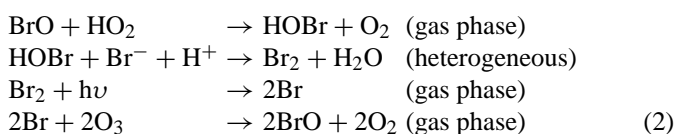
1 Introduction

Sudden loss of ozone in the tropospheric boundary layer in polar spring has been well known in the Arctic since the 1980s (e.g. Barrie et al., 1988), and has now been observed in the Antarctic (Kreher et al., 1997), where the sparse location

of measurement sites means that the ozone-poor air is often lifted above the boundary layer by the time it arrives at the site (Wessel et al., 1998; Roscoe et al., 2001). At first there was some speculation that the Arctic ozone loss might be anthropogenic in origin, but it is now known to be a natural process catalysed by bromine compounds. The ozone loss is accompanied by a simultaneous increase in BrO (McConnell et al., 1992; Platt and Lehrer, 1997), which removes ozone via which removes ozone via the gas-phase reactions:



The BrO originates from Br ions in sea salt (Tang and McConnell, 1996) via reactions that multiply the reactive bromine compounds in the gas phase once the process has been started (e.g. Vogt et al., 1996), in the so-called “bromine explosion”:



plus other channels involving Cl^- and BrCl .

There is only about $0.5 \times 10^{13} \text{ molec cm}^{-2}$ of BrO in the troposphere over the mid-latitude open ocean (Leser et al., 2003), whereas polar enhancements of tropospheric BrO in spring exceed $4 \times 10^{13} \text{ molec cm}^{-2}$ (e.g. Richter et al., 1998), so there must be a process to concentrate the number density or surface density of Br ions compared to sea water, or a

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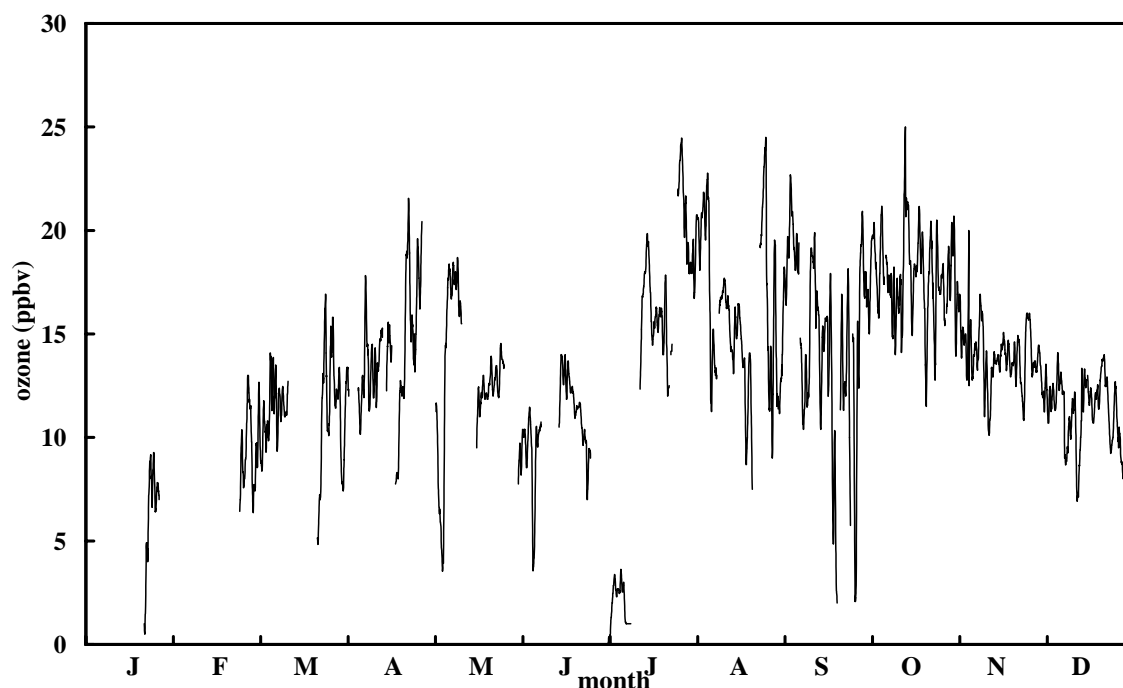


Fig. 1. Hourly measurements of surface ozone at Halley (75.6° S) in 1958, smoothed by a 13-point running mean (about half a day) so that features can be seen in a whole-year plot. Note the rapid rise from small values each time the instrument had been switched off, the lengthy periods of reduced ozone in June and July, and the short periods of reduced ozone in August and September.

different priming process, before the bromine explosion can start. Near the poles, concentration occurs during freezing of sea ice, which expels brine upwards as well as downwards. The upper brine is contained in pools of slush, and can be wicked above the slush surface by the frost flowers that form on fresh sea ice (Rankin et al., 2002).

Tropospheric ozone has a long replacement time in spring in the Antarctic because of the unpolluted atmosphere, hence the ozone-poor air which reaches the free troposphere may become well mixed and may have a small positive climate feedback during global warming (Roscoe et al., 2001).

In this paper, we examine the surface ozone record from the first station at Halley Bay (75.5° S) in 1958, and show that many characteristics of the record are similar to those we observe today, so that it is quite believable. We show that sudden ozone loss occurred in spring, as is also now observed, but loss also appeared to occur in midwinter during total darkness, which we would not expect because the above BrO production cycle cannot proceed in the dark. We correlate the ozone loss episodes with local meteorological conditions, and we discuss possible explanations for the midwinter loss.

2 Measurements and their quality in 1958

A base at Halley Bay was established in January 1956, and a fully functioning station in January 1957, by the Royal So-

ciety Expedition as a contribution to the International Geophysical Year, which lasted from July 1957 to June 1958. Like all stations at Halley, the base was constructed on the floating ice shelf, but was only about 2 km from the nearest possible open water (Brunt, 1964, p. 11), whereas recent stations have been 12 to 20 km away. A broad range of routine geophysical measurements was established by 1957, including meteorological parameters and total ozone measurements (Brunt, 1962, 1964) that continue to this day.

In 1957 and 1958, meteorological variables such as temperature, wind speed and direction, as well as solar and infrared radiation, were measured by the standard sensors of the time. Some had electrical recorders, and some were read by eye with results noted by hand at intervals of 3 h or less. Printed tables of temperature, wind speed, wind direction and cloud (Brunt, 1964) have since been entered into computer archives at the British Antarctic Survey (BAS), where they have undergone the usual quality control checks for continuity and range. Tables of hourly fluxes of solar and total radiation were also printed (Brunt, 1962), and we have entered some of these into computer files.

An addition in 1958 was a sensor of surface ozone. The sensor was designed and built at the Clarendon Laboratory, and was similar to the 16 ozone sondes successfully flown on balloons at Halley in 1958 in being a prototype of the later Brewer-Mast sonde (Brewer and Milford, 1960). Like the more recent ECC sonde (Komhyr, 1969), they functioned by the reaction of ozone with KI solution, but the arrangement

of electrodes and polarisation differed. In fact two prototype designs each with differing arrangements are described by Brewer and Milford (1960). The Halley instruments were of the earlier “transmogripher” design, where solution flowed from cathode to anode to prevent the return of the re-formed iodine to the cathode. Compared to the balloon-borne sondes, the sensor designed for surface ozone measurements had a longer cathode and a greater air flow (0.3 L/min), to increase its sensitivity, and had a pressure-independent flow controller (Brunt, 1962). It was installed in the south-east end of the loft of the main hut, and air was drawn from outside via 1.5 m of polyethylene tubing which terminated 0.25 m above the roof. It was 1.8 m above the nearby snow and 4.2 m above the main ice shelf in January 1958, but by November 1958 snow had accumulated such that these heights were only 0.2 m and 3 m, respectively. The base had no potential interfering devices or structures in the most frequent upwind directions (E, WSW). Occasionally, light NE winds blew past the nearby diesel generator, and so contained very little ozone. These values were excluded from the printed tables, but were later used as a check of zero (see below).

Just before entering the sensor, air passed through a short quartz tube that could be heated to 300°C to remove ozone, thereby enabling the zero of the sensor to be measured hourly (until 26 July when it broke, after which episodes of light NE wind passing the diesel generator had to be used). A mercury lamp, whose UV light created ozone in nearby air, was used to generate ozone from time to time in order to check that there was no total failure of the sensor. Until 23 February, the current from the sensor was read from a galvanometer and recorded by hand, thereafter it was amplified and recorded on a chart. Supplies of chemicals were insufficient for continuous measurements for the year, so stocks were rationed to about 20 days/month until August. Earlier in the year, the capillary in the flow controller frequently became blocked and was removed for cleaning. Hourly mean values were extracted by hand at the time from the electrical recordings, eliminating gaps for stoppages and calibration, and tabulated in Brunt (1962). We have now entered the values from the tables into a computer file, and Fig. 1 shows them for the year.

The envelope of maximum ozone is an annual cycle, which ranges from 10 ppbv in January to 22 ppbv in August. Given the prototype nature of the sonde and the potential for ozone loss on the inlet to the system in those pre-*teflon* days, we must question its calibration. In this design, the total variation of output current over the full nominal range of various instrument parameters was 5% for the voltage applied to the electrodes, 5% for the rate of air flow with constant rate of ozone flow, and 10% for the rate of solution flow (Brewer and Milford, 1960, Figs. 3a, 4b and 5a). At Halley, the gain and linearity of the amplifier was checked between 10 and 40 times per month, and the monthly mean was found to be stable within 1% with a maximum variation within each month

of $\pm 4\%$, with a non-linearity of 2% – such checks were important in those days of amplifiers with low open-loop gain. Occasionally the automated flow-control valve jammed, and the variation of sensor output with pressure across its capillary was then used to check the linearity of the whole system, which was certainly accurate within 10% (Brunt, 1962, p. 80). The flow rate for a given pressure across the capillary had been determined in UK before shipment, other calibration factors were derived from the standard formula for the current generated by ozone from iodine ions in solution.

We can also consider the calibration quality by comparing the values with measurements by more modern instruments in Antarctica. In recent years there are many measurements of surface ozone at Neumayer, also a coastal site, and South Pole station started measurements of surface ozone with a modern instrument in late 1974. Figure 2 shows monthly-mean data from South Pole from 1975 to 1977 (Hoffman, 1996), together with some recent Neumayer data (WDCGG, 2003) as well as the Halley data. In Fig. 2 we have multiplied the South Pole values by 0.94 to account for the 6% increase in mixing ratio expected at its altitude of 2.8 km (mixing ratios of ozone in the free troposphere measured by ozonesondes at Halley in 1987 usually increased by between 2% and 2.5%/km, Gardiner and Farman, 1988).

Comparing data from Neumayer and South Pole in Fig. 2, it is clear that the annual cycle at the coastal station of Neumayer differs from that of the inland South Pole, with similar values in winter but smaller values at the coast in summer (January), so the small values in summer at coastal Halley are not evidence of a threefold calibration error at Halley.

Figure 2 shows another curve with the Neumayer values multiplied by a factor chosen by eye to fit the maxima of the Halley data. The factor varies linearly through the year, starting at 0.65 and ending at 0.85. This suggests several possibilities:

- there has been a general increase in surface ozone in Antarctic since 1958, as elsewhere but smaller, perhaps because partly polluted air is now there from mid-latitudes
- transport of partly polluted air may be larger in summer than in winter
- alternatively, the calibration of the Halley measurements is about 35% low at the start of the year and about 15% low at the end.

Currently we have little information to distinguish these possibilities, but a calibration accurate to 15% for the small values of ozone in the troposphere would be considered fairly good for a modern chemical ozonesonde. Even with the large values in the stratosphere, the calibration of an ECC sonde varies by 5 to 10% depending on the strength of the solutions and the type of buffers in the solution (Johnson et al., 2002).

If possibility (c) above is correct, it also suggests long-term conditioning of the inlet. Conditioning is a process

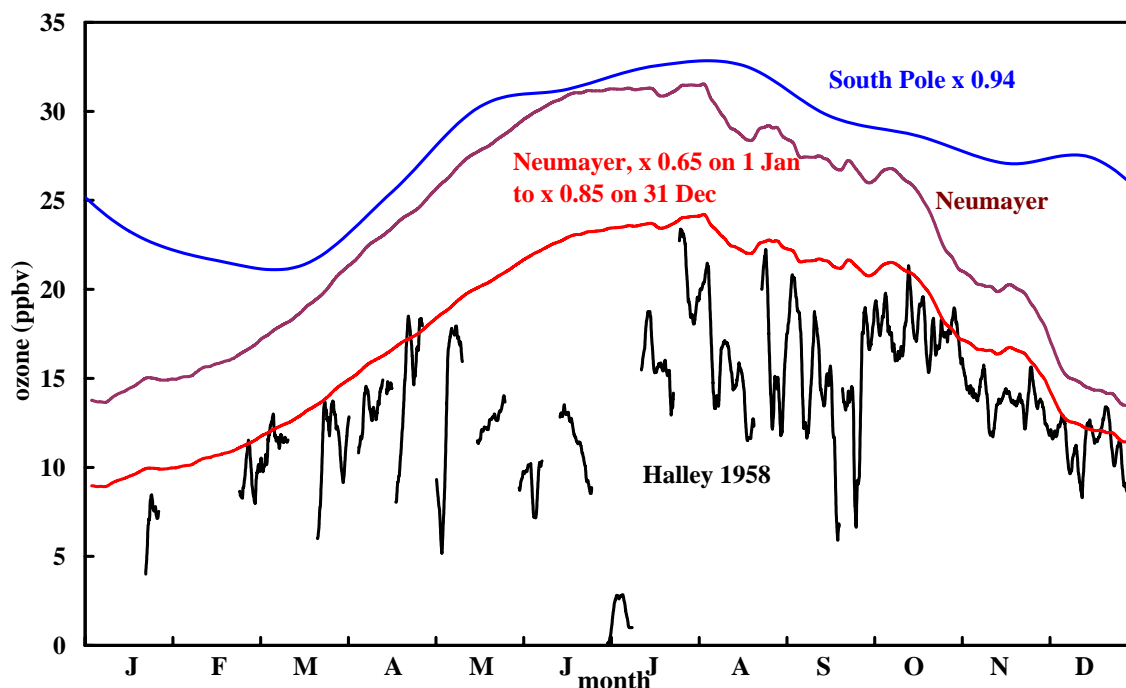


Fig. 2. The hourly measurements of Fig. 1 at Halley, but smoothed by a 49 point running mean to reduce clutter on the plot whilst retaining important features (black), together with monthly-mean surface ozone at S Pole from 1975 to 1977 multiplied by 0.94 to approximate the values we expect at sea level (blue), and surface ozone measured at Neumayer averaged from 1999 to 2001 and smoothed by a 16-day running mean to show the annual cycle (brown). To illustrate either long term changes in ozone since 1958 plus site-specific differences, or possible calibration errors at Halley, Neumayer values are also multiplied by a factor changing linearly throughout the year from 0.65 to 0.85 (red). The red curve is chosen to approximate the maxima in the Halley 1958 values.

where any reactive surfaces and reactive surface contaminants are neutralised by reacting with ozone. Typically these would be hydrocarbons from skin or from machining, and plasticizers within a surface layer of non-teflon components. Exposing them to enough ozone-containing air oxidises these layers and contaminants so that they no longer remove ozone. Surfaces that catalyse $2\text{O}_3 \rightarrow 3\text{O}_2$, such as aluminium alloys, cannot be conditioned as the reaction proceeds indefinitely. After conditioning, surfaces may become re-contaminated, but the inner surface of tubing is unlikely to do so unless handled or stored in a hydrocarbon-rich environment. Conditioning of the inlet and pump of modern ozonesondes is undertaken routinely a few days before flying them in order to eliminate any period of stabilisation (Kohmyr, 1969), and takes less than an hour because modern components are teflon, because the inlet length is only 200 mm, and because several hundred ppbv of ozone is added to the conditioning air. Sondes remain conditioned for many days if stored in a normal laboratory environment, without special precautions.

We can observe such a short-term conditioning process for the 1958 sensor with ambient ozone, by examining the measurements after stoppages, shown in Fig. 3. The time for short-term stabilisation cannot be determined exactly because the ozone was not necessarily constant, as is obvious from the figure. However, it is clear by eye that the condi-

tioning process takes many hours but less than 3 days. This is a reasonable range of values for a polyethylene inlet of length 1500 mm. Figure 3 only shows restarts after 10 or more days of no measurements, shorter periods did not seem to display conditioning, except possibly the 8-day period at the end of June discussed in Sect. 4. Such a period would be rather short for teflon components, but we presume that plasticizers within polyethylene tubing are able to migrate to the surface on such a timescale, so that the surface must be re-conditioned anew. Such behaviour of plasticizers might also be responsible for the long-term conditioning that seemed to occur. The result from Fig. 3 means that the first 3 days after 8 or more days of no measurements should not be used for quantitative work, a recommendation we follow in Sects. 3 and 4 below.

The comparatively well-conditioned nature of the inlet system, once running, is also supported by the linearity of the response when varying the pump speed (Brunt, 1962, p. 80). This test was possible because of occasions when the flow control jammed but could be freed without dismantling the system. The test was used at the time to illustrate the linearity of the system, but with hindsight we can say it also demonstrates the adequacy of its conditioning – the time-dependent ozone loss of an ill-conditioned system would produce loops and curves in a linearity plot. In the plot, the scatter about

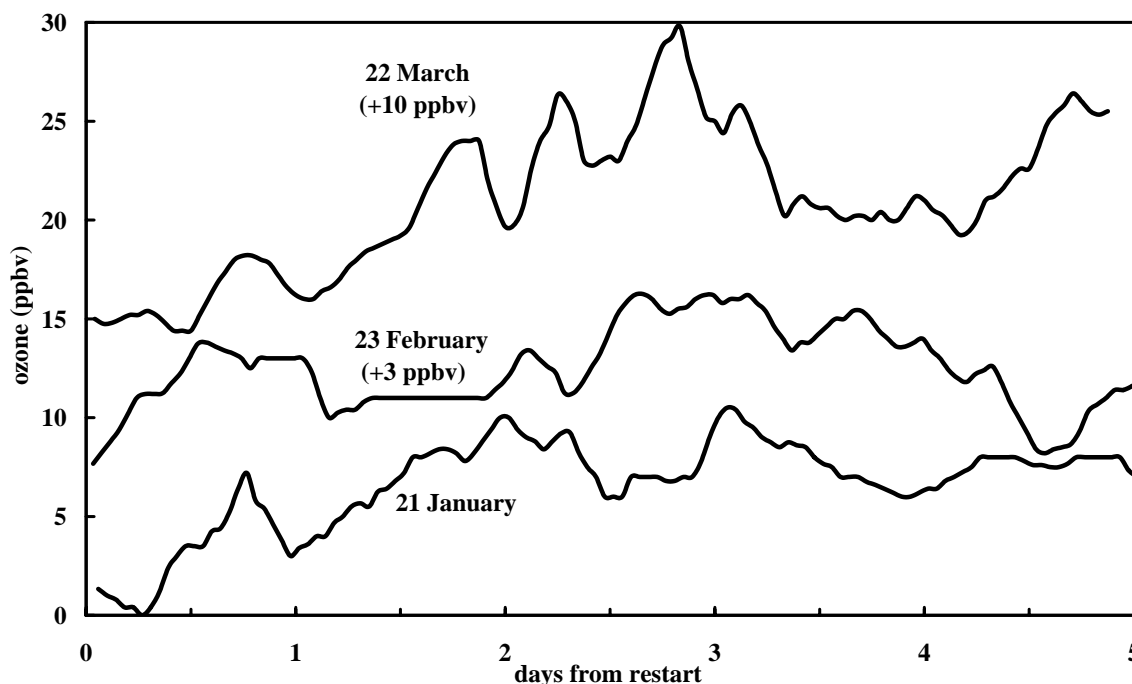


Fig. 3. Surface ozone measurements at Halley in 1958 after starting or restarting the ozone sensor on the three occasions when the sensor had been off for many days (21 January, 23 February, 22 March – other off periods were rather shorter except before 29 June). The curves for 23 February and 22 March are offset by 3 and 10 ppbv for clarity, and the hourly recordings are smoothed by a 5-h running mean to help guide the eye and ensure that the curves do not overlap. The time for stabilisation or conditioning is seen to be between 0.5 and 2 days.

a straight line through the origin was about 5% of the maximum signal (1-sigma) over a ten to one range of signal, and the points were evenly distributed with no curvature obvious to the eye.

In summary, despite initially frequent problems with the flow controller and other system components, the surface ozone sensor was operated for many days at a time with frequent subsystem calibration checks, and measurements obtained during flow-control problems were used to check linearity of the system as a whole. Measurements obtained whilst these problems were occurring were not included in the tabulated values. Later in the year, measurements were near-continuous apart from subsystem calibration checks.

To conclude, the surface ozone sensor was operated with care throughout 1958, and we should not discount the results merely because it was over 40 years ago.

3 Loss of surface ozone in spring

Figure 1 shows two or three short periods in September when ozone values decreased rapidly to near-zero, and a similar number in August when ozone values were rapidly halved. These episodes are shown in more detail in Fig. 4, together with meteorological parameters. These ozone-loss episodes follow a scenario now familiar in the Arctic (e.g. Barrie et

al., 1988), and now observed in the Antarctic (Wessel et al., 1998; Roscoe et al., 2001; Friess et al., 2004):

- ozone decreases in less than a day, the value remaining small for between a few hours and a few days before increasing rapidly to its previous value;
- the decrease coincides with wind from the sea-ice zone, the increase coincides with the wind changing direction;
- episodes occur in the spring, after sunrise over the sea-ice zone from which the wind is blowing.

In Fig. 4a, ozone decreased from 18 to 2.3 ppbv during the second half of 17 September. The wind was from the east, which at Halley usually means that it has blown from some distance over the sea-ice zone during a synoptic storm passing to the north. Unfortunately, whether the air had contacted the sea-ice surface would need trajectory calculations from meteorological reanalyses, not available for 1958. A low frequency of trajectories that contact the surface of the sea-ice zone and the surface at Halley during synoptic storms, as observed at McMurdo and Neumayer in 1995 (Roscoe et al., 2001), would explain the few such episodes at Halley in Fig. 4.

In Fig. 4a on 19 September, ozone decreased similarly rapidly to 2 ppbv, coincident with winds changing to the west with speeds of 10 knots or less. In winter and spring there is

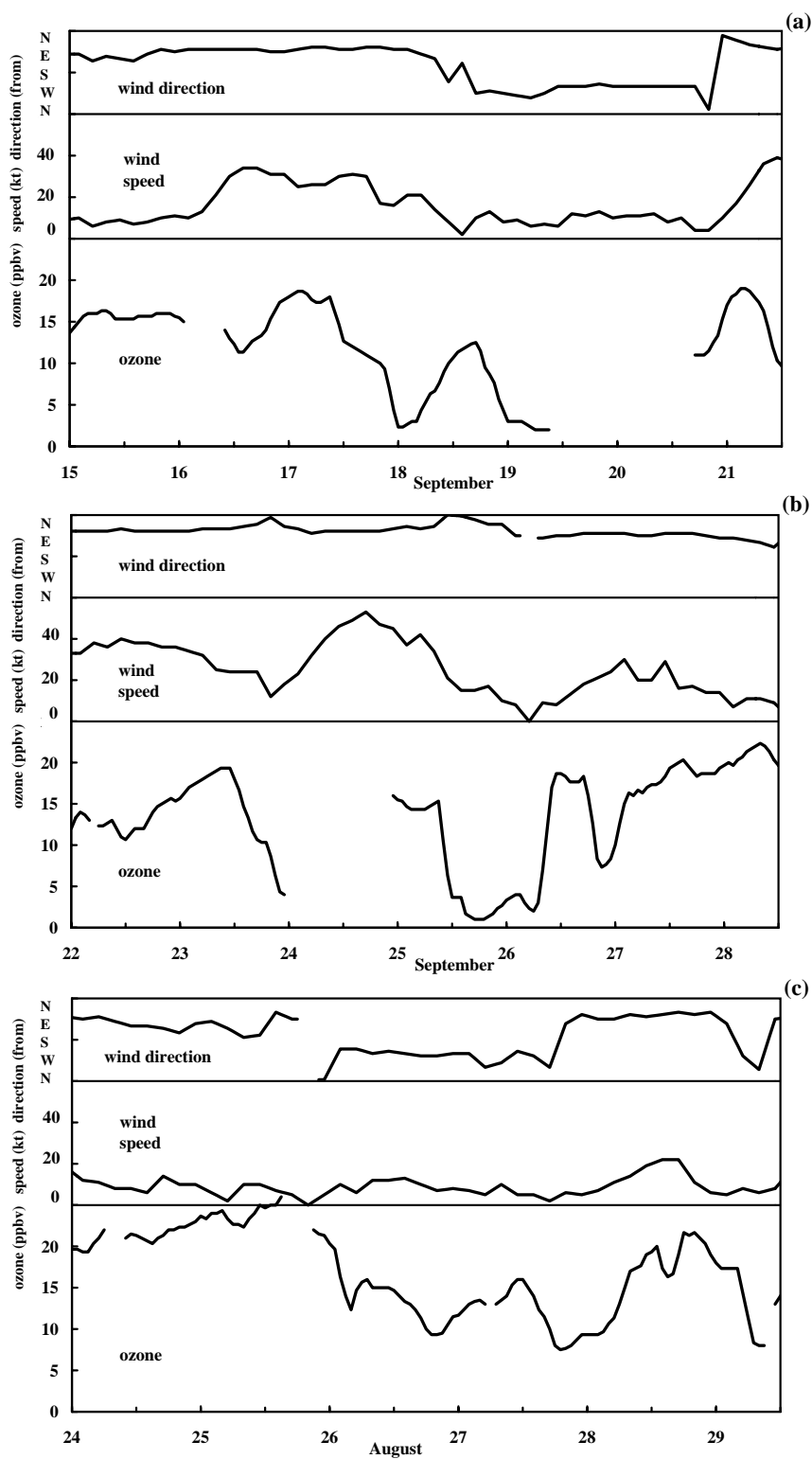


Fig. 4. Surface ozone, wind speed and direction, measured at Halley in 1958, during periods in spring when ozone decreased rapidly, (a) from 15 September, (b) from 22 September, (c) from 24 August. The hourly ozone values are smoothed by a 3-point running mean for consistency with the 3-hourly meteorological parameters. Small ozone values mostly occur during lighter winds from the west or the north to north-east. In September they go below 3 ppbv, as observed in recent episodes of polar surface ozone loss 3 months after midwinter.

a frequent area of open water (a polynya) many tens of km in diameter at Precious Bay (Anderson, 1993), which extends northwards to points about 20 km away from the 1958 base at an angle of a few degrees south of west and about 30 km away at an angle of a few degrees north of west. A wind of 10 knots is characteristic of weak synoptic flow, which would be expected to preserve ozone-poor air in transit, without significant dilution, for such a distance. Although some ozone data is missing, ozone values returned to normal when the wind reverted on 21 September, consistent with this interpretation.

In Fig. 4b, the two ozone-loss episodes (23 and 25 September) occur similarly rapidly but arise when the wind direction changed to the north or north-east. We expect frequent patches of open and freshly-freezing water close to Halley to the north in September.

In Fig. 4c, ozone loss occurred on 26 August about half a day after the wind veered from the east to coming from the west at speeds below 10 knots, and recovered 2 days later with a similar delay after the wind returned and increased towards 20 knots. A second short episode on 29 August was more synchronous with wind direction, again from the west. In both episodes, only half the ozone was lost. Hence either the source of ozone-poor air was further away than in September, allowing a delay and mixing with undepleted air, or there was a nearby source of BrO-rich air to the west (such as Precious Bay) but there was insufficient UV sunlight this early in the spring for rapid and total depletion.

When first discovered in the Arctic in the 1980s, although some workers correctly speculated that the surface ozone loss was a natural process involving halogens, there was also some speculation that the process was associated with anthropogenic pollutants, particularly sulphuric acid aerosol (e.g. Fan and Jacob 1992). These measurements at Halley in 1958, which would have instantly dispelled such a notion, had meanwhile been forgotten.

4 Apparent loss of surface ozone in midwinter

Figure 1 also shows very small ozone values for almost a week in July, expanded in Figs. 5a and b. The question arises, can we discount these measurements due to some problem with the apparatus? We must be suspicious of a problem with apparatus because:

- (a1) the apparatus was off for 6.5 days before the event, and so the inlet became badly conditioned;
- (b1) there are also reductions in ozone in May and June in Fig. 1, which would be consistent with a problem with the apparatus during colder temperatures;
- (c1) recorded values on 8 July were the smallest for the longest duration in the whole year's data set;
- (d1) this occurred in the middle of the winter dark, when morale could well be low.

We might also be suspicious that

- (e1) exhaust from the generator reached the inlet because winds were light

However, there are important counters to each of these suspicions.

- (a2) The detail in Fig. 5 shows that, after being switched back on early on 2 July, there was a recovery during the following two days to 3.7 ppbv – reconditioning had proceeded as usual after switch-on, as in Fig. 3. The smallest ozone values were recorded over 3 days after the reconditioning was complete.
- (b2) Small ozone values were already evident by 5 July, well before temperatures reached their minimum; and in mid-August temperatures were also colder than -40°C , only a few degrees warmer than on 8 July, but ozone values were greater than 10 ppbv (see Fig. 6). If we plot the probable ozone deficit for the whole year we also find no correlation with temperature (Fig. 7). If the solution were to start to freeze, this would reduce the rate of solution flow from cathode to anode, but laboratory measurements (Brewer and Milford, 1960, Fig. 5a) showed that the output was almost constant over a large range of flow rates (30 to 1), and that the sensitivity to ozone initially increased a little as flow rates were reduced.
- (c2) The sensitivity of the sensor to ozone in early July was specifically confirmed by testing with the mercury lamp that produces ozone (Brunt, 1962, p. 79).
- (d2) During the full moon after midwinter, the same personnel made the largest concentration of lunar Dobson measurements of the whole winter period – morale must have been high to make so many of these difficult measurements.
- (e2) On 8 July when ozone values remained close to zero, winds reached 20 knots from the SW, the opposite direction to the generator

Hence we can find no specific reason to discount the recorded values in July, each of the obvious possibilities can be discounted, and we stress again that the sensor was operated with care so we should not discount results merely because it was over 40 years ago. However, we must remain suspicious that there was a problem with the apparatus because no such low-ozone episodes are observed in midwinter at Neumayer. It may be that the probability of freshly freezing sea ice close to Neumayer in winter is much less than at Halley, particularly than at Halley in 1958 when the base was very close to the northern edge of the ice shelf, but the suspicion must remain.

Setting this suspicion aside by taking the midwinter results at their face value, we can speculate about the rate of ozone loss. Taking into account the period when the sensor

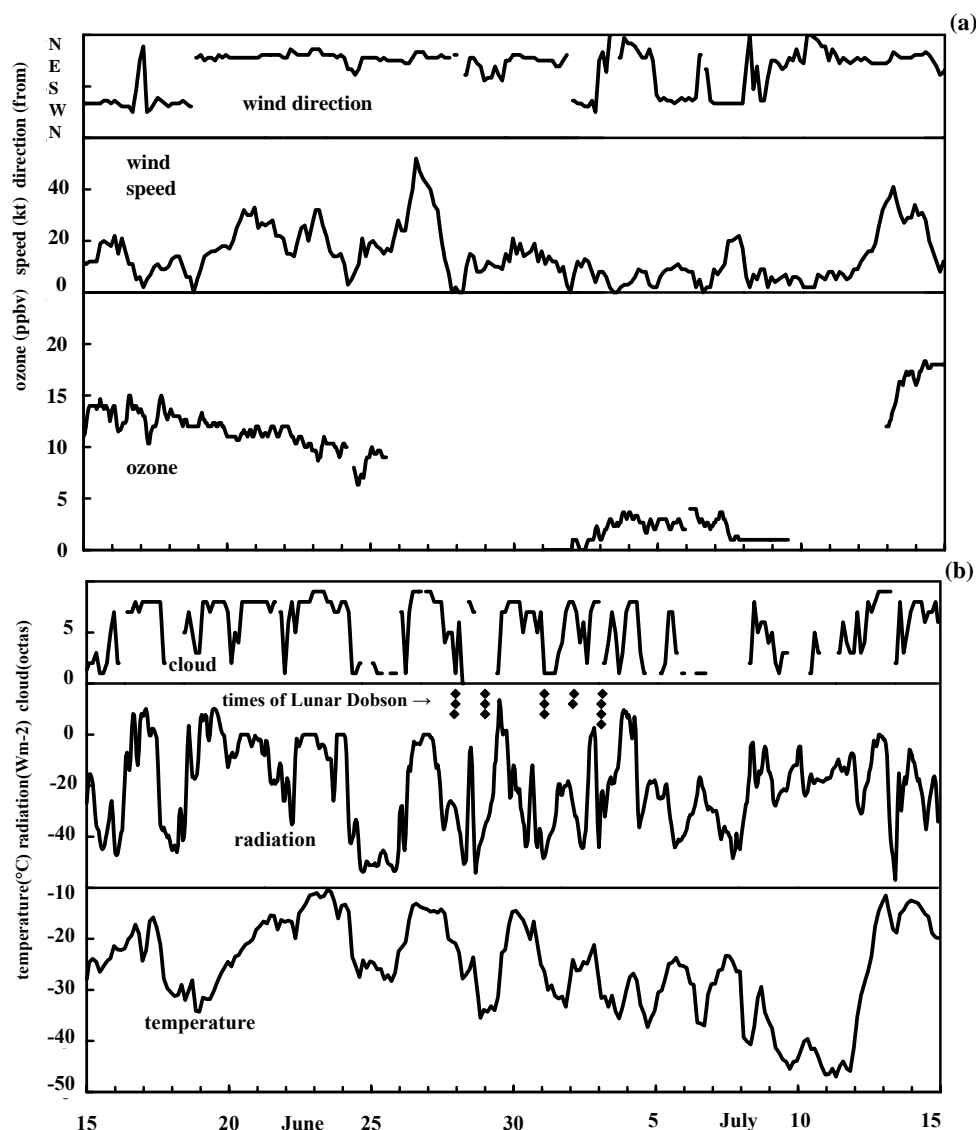


Fig. 5. Measurements at Halley in 1958, during the period in midwinter when ozone appeared to decrease to a very small value, **(a)** of surface ozone, wind speed and direction **(b)** of cloud, surface temperature, net flux of radiation at the surface, and times when the Dobson spectrophotometer observed the moon. The hourly ozone and radiation values are smoothed by a 3-point running mean for consistency with the 3-hourly meteorological parameters. The Lunar Dobson points (♦ – see text for relevance) are separated vertically by an arbitrary amount so as to distinguish measurements closely-spaced in time. The very small surface ozone readings occurred during a 9-day period of lighter winds that mostly veered between the south-west and the north, coincident with frequent shorter periods of little cloud, large radiative cooling and cold temperatures.

was off plus the reconditioning period apparent in Fig. 5, the minimum rate of decrease would have been from 9 ppbv to 3.7 ppbv in 9 days. Hence we conjecture a minimum rate of ozone loss of 0.6 ppbv/day.

The snow near the modern base of Halley is very clean and non-conducting, such that low-frequency radar antennas can be left on the surface where they can become buried by several metres of snow accumulation without loss of signal. Ozone removal on snow was measured by Galbally and

Roy (1980) to be very dependent on cleanliness, the cleanest they could find at mid-latitudes giving a deposition velocity of 4×10^{-5} m/s, which should therefore be regarded as an upper limit for Halley (the destruction of ozone on pure ice corresponds to a deposition velocity 50 times smaller, Langenberg and Schurath, 1999). In winter at Halley, a typical boundary-layer thickness is 400 m (King and Turner, 1997), so this upper limit would correspond to an initial removal rate from 15 ppbv of 1.5×10^{-6} ppbv/s or 0.13 ppbv/day. This is

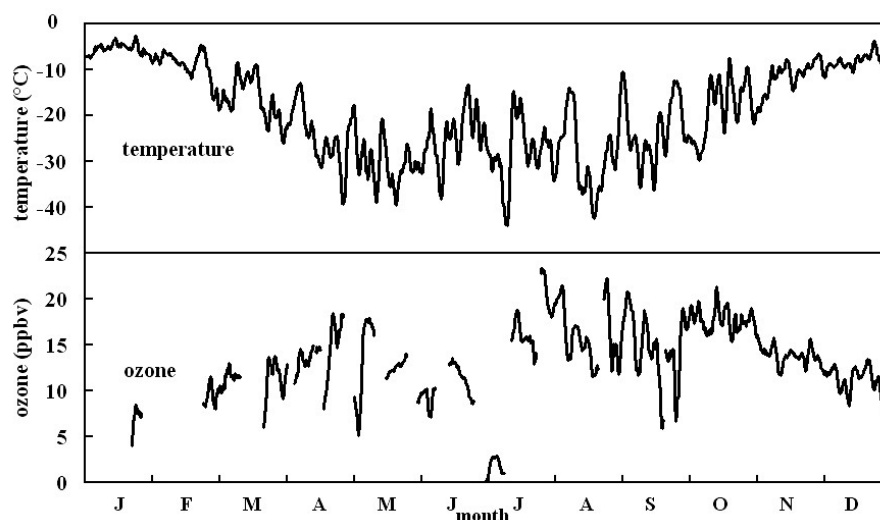


Fig. 6. Hourly measurements of surface ozone at Halley in 1958 smoothed by a 49-point running mean, together with the 3-hourly temperature smoothed by a 17-point running mean, so that each is smoothed by about 2 days. Temperatures in mid-August were colder than -40°C but ozone values were greater than 10 ppbv, suggesting that the ozone values less than 5 ppbv in early July were not an instrument malfunction due to the similarly cold temperatures in July.

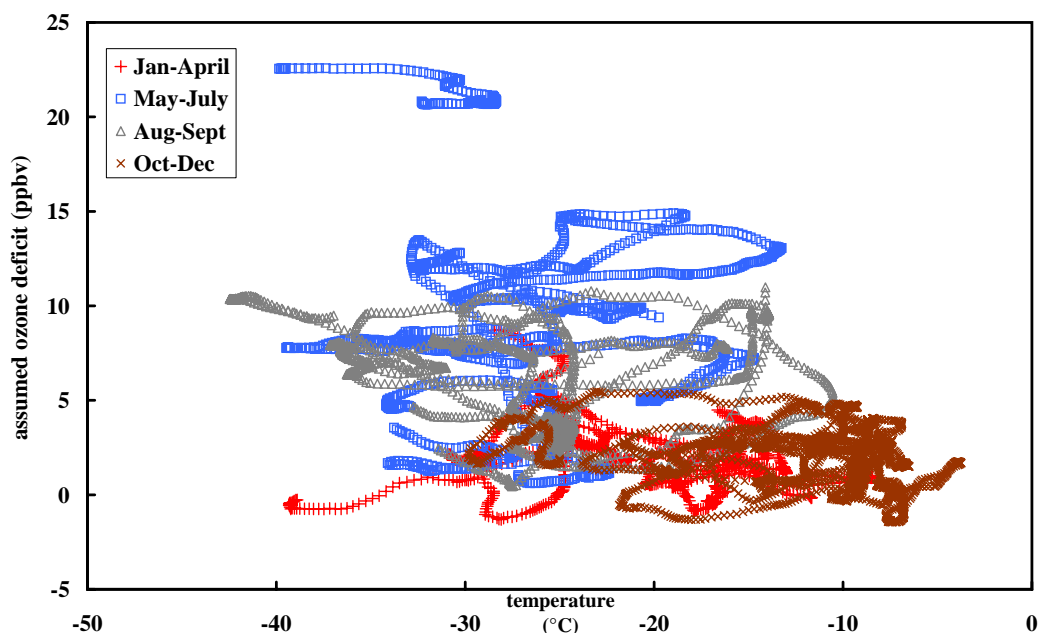


Fig. 7. Scatter plot of assumed ozone deficit versus temperature, at Halley in 1958. The ozone deficit is assumed to be the difference between the black and red curves in Fig. 2. Low-ozone episodes in September and the restarts illustrated in Fig. 3 are excluded. There is no obvious correlation in the data set as a whole, nor in any of the individual periods shown – the reduced ozone in early winter and the low ozone in midwinter are not caused by cold temperatures at the measurement site.

less than a quarter the minimum removal rate in 1958 conjectured above, far too slow. Other reports of ozone removal within the snowpack (e.g. Peterson and Honrath, 2001) demand sunlight, and so would not apply in the midwinter dark.

The catalytic removal of ozone by BrO in Eq. (1) has one pathway which functions without light, but the production of

large amounts of BrO from Br ions in Eq. (2) needs light. A mechanism is needed to create BrO from seawater or sea ice in the dark, or to remove ozone in the presence of seawater or sea ice in the dark.

A dark reaction of sea-salt and ozone has been observed in the laboratory by Hutterli et al. (2005), and the details

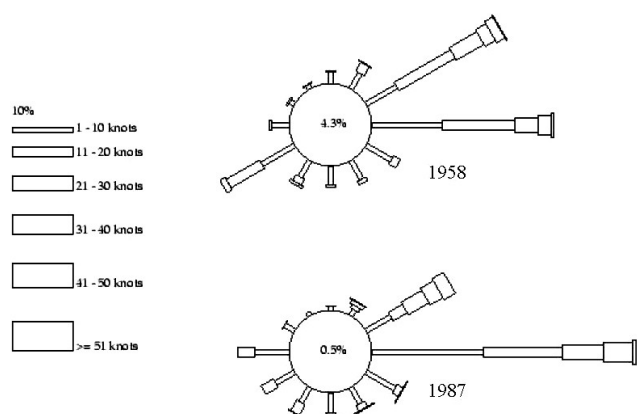
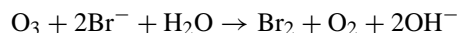


Fig. 8. Wind roses at Halley from 1 May to 15 July in 1958 (top) and in 1987. The length of each segment is proportional to the accumulated duration in that direction, the width of each segment is proportional to its wind speed. Note lower frequency in 1987 of all winds from the south-west, where there is frequent open and freshly freezing water in winter.

of a dark reaction with seawater ice were observed in the laboratory by Oum et al. (1998). In the latter study, Br_2 was produced from seawater ice in the presence of ozone, the amounts produced being approximately proportional to ozone. This suggested that reactions with ozone were occurring, and the authors proposed a reaction sequence with the net result:



together with other reactions involving chloride ions. Following their estimation of the amount of Br_2 produced and so of ozone lost, a boundary layer of depth 100 m over a large area of seawater ice would lose 5.8 pptv of ozone/day. This is 1/100 of the minimum removal rate in 1958 of 0.6 ppbv/day conjectured above. Factors that could amplify the loss rate are:

- The salinity of brine expelled to the surface during the seawater freezing process commonly reaches 3 times that of seawater (Rankin et al., 2002). But collection was usually in temperatures above -25°C when it was safer for the collecting personnel. It is also possible that the brine may have been collected as slush containing ice, which would have melted before the analysis, so diluting the brine. In principle, the fractionation process can create brine of many times this salinity, particularly in colder conditions.
- The surface area of frost flowers is obviously larger than that of the ice surface they cover (Rankin et al., 2003, Fig. 2). Although Domine et al. (2005) only measured an amplification factor of 1.4, their frost flowers were physically small and widely spaced – characteristic of growth in warmer conditions. In winter near Halley

the temperatures may have reached -45°C , much colder than any field or laboratory studies. Examination of photographs suggests that amplifications of 10 should easily be achieved, and more is possible.

Hence a total amplification could range from a minimum of 4.2 to a value of at least 30, and the necessary value of 100 cannot be excluded although is perhaps the maximum credible. If so, there would have to be little dilution of the effect during transport of the air mass to Halley, so it would be essential to be close to large amounts of freshly freezing water in the direction from which light winds blow during the loss period.

This is indeed the case:

- in winter there is a frequent area of open water (a polynya) many tens of km in diameter at Precious Bay (Anderson 1993), whose closest point to the south-west is only 20 km away;
- there is often a lead of open water at the shore in winter, of width a few hundred metres, only 2 km to the north in 1958.

Figure 5a shows that these are the frequent directions of the wind during the period of very small ozone values (2 to 9 July), and the wind was less than 10 knots for most of the period, occasionally falling below 2 knots.

Figure 5b shows that cloud was frequently reported 1/8 between 1 and 6 July. However, the ability to discern clear skies during winter at Halley, where aurora are frequent, is notoriously difficult; and 1/8 is reported if any cloud is visible in any part of the sky, so skies could well have been clear. Furthermore, Fig. 5b shows many Lunar Dobson measurements at the end of June and beginning of July, far more than at most full moons. This may be partly because of the long duration of moonlight (24 h on 2 July), but it also suggests frequent clear skies as these are difficult measurements if the moon is partially or occasionally obscured. There were simultaneous episodes of large radiative cooling, also suggesting clear skies. There was also a period of large radiative cooling, again suggesting clear skies, throughout 7 July. Frequent and prolonged clear skies suggests an extensive stable boundary layer, with little chance of dilution of ozone-poor air coming from nearby areas of freshly freezing water.

If the midwinter low-ozone values are genuine, why are they not observed in early winter at Neumayer during the many years of observation of surface ozone in the 1990s (WDCGG, 2003), the more so as Neumayer is only 700 km NE of Halley on the same Weddell Sea coast, and the relative wind roses are almost identical (Konig-Langlo et al., 1998)? Perhaps this is because the area of frequent open water in winter near Neumayer is only about 1/10 that near Halley (Arrigo and van Dijken, 2003) – there is less potential for frost-flower formation close to Neumayer in winter. This is consistent with the annual pattern of sea-salt aerosol arriving

at each station, which has a pronounced maximum in winter at Halley but has little consistent variation at Neumayer (Wagenbach et al., 1998).

If the midwinter low-ozone values are genuine, why were they not observed at Halley during 1987, when ozonesonde measurements included near-surface values (Gardiner and Farman, 1988)? Perhaps because in early winter in 1987, the wind directions were very different, as shown in Fig. 8 – in 1987, there was very little wind from the west. Furthermore, only 5 ozonesondes were deployed in June and July, with unequal spacing, so that any midwinter low-ozone episode might well have been missed.

5 Conclusion

Measurements of surface ozone were made at Halley during 1958. The zero of the measurement was frequently checked, the calibration appears to be reliable, and the inlet became well conditioned within three days of restarting the pump. The measurements show:

- (a) an envelope of maxima with an annual cycle from 12 ppbv in February to 25 ppbv in August, of similar shape to recent values at Neumayer, but about 35% less at the start of the year and about 15% less at the end
- (b) short periods in spring (September) when ozone values decreased rapidly to near-zero, such as later observed to be widespread in spring in coastal regions near either pole
- (c) apparently very small ozone values for over a week in midwinter (July)

If these 1958 measurements had been remembered when ozone-loss episodes in spring in the Arctic were first discovered in the 1980s, they would have dispelled speculation that the Arctic episodes were anthropogenic in origin. Unfortunately, their only publication in the open literature was a summary paper of meteorological, glaciological and seismological measurements from the Royal Society expedition (MacDowall, 1960). The paper had less than 3 pages devoted to the surface ozone measurements, only showed the monthly mean values, and did not include “ozone” or “chemistry” in its title.

The small values recorded in midwinter cannot be discounted for any obvious reason such as low temperatures. In midwinter, the flow rate was normal and the sensitivity of the sensor to ozone was confirmed by creating ozone by means of a mercury lamp. We must remain suspicious of these small values because they were not observed in midwinter at Neumayer in the 1990s nor at Halley in 1987, although there is less open water in winter near Neumayer and the wind direction differed at Halley in 1987. If we accept these small values in 1958, the minimum rate of removal in midwinter dark is consistent with laboratory measurements of the dark

reaction with sea ice, provided we postulate a large enough amplification of salinity and area, for example by frost flowers.

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References

- Anderson, P. S.: Evidence for an Antarctic winter coastal polynya, *Antarctic Sci.*, 5, 221–226, 1993.
- Arrigo, K. R. and van Dijken, G. L.: Phytoplankton dynamics within 37 Antarctic coastal polynya systems, *J. Geophys. Res.*, 108(C8), 3271, doi:10.1029/2002JC001739, 2003.
- Barrie, L. A., Bottenheim, J. W., Schnell, R. C., Crutzen, P. J., and Rasmussen, R. A.: Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, *Nature*, 334, 138–141, 1988.
- Brewer, A. W. and Milford, J. R.: The Oxford-Kew ozone sonde, *Proc Roy. Soc. London*, A256, 470–495, 1960.
- Brunt, D.: The Royal Society International Geophysical Year Antarctic expedition, Halley Bay 1955–1959, Volume III, seismology, meteorology, edited by: Brunt, D., The Royal Society, London, 1962.
- Brunt, D.: The Royal Society International Geophysical Year Antarctic expedition, Halley Bay 1955–1959, Volume IV, meteorology, glaciology, appendixes, edited by: Brunt, D., The Royal Society, London, 1964.
- Domine, F., Taillandier, A. S., Simpson, W. R., and Severin, K.: Specific surface area, density and microstructure of frost flowers, *Geophys. Res. Lett.* 32, L13502, doi:10.1029/2005GL023245, 2005.
- Fan, S.-M. and Jacob, D. J.: “Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols”, *Nature* 359, 522–524, 1992.
- Friess, U., Hollwedel, J., König-Langlo, G., Wagner, T., and Platt, U.: Dynamics and chemistry of tropospheric bromine explosion events in the Antarctic coastal region, *J. Geophys. Res.*, 109, D06305, doi:10.1029/2003JD004133, 2004.
- Galbally, I. E. and Roy, C. R.: Destruction of ozone at the earth’s surface, *Quart. J. R. Met. Soc.*, 106, 599–620, 1980.
- Gardiner, B. G. and Farman, J. C.: Results of the 1987 ozonesonde programme at Halley Bay, Antarctica, BAS, Cambridge, ISBN 0-85665-128-1, 1988.
- Hoffman, D.: Climate Monitoring and Diagnostics Laboratory, No. 23 Summary Report 1994–95, edited by: Hoffmann, D. J., U.S. Dept Commerce, 1996.
- Hutterli, M. A., Rankin, A. M., Jones, A. E., Knox, K. J., and Wolff, E. W.: A laboratory study of ozone depletion over frost flowers, *Geophys. Res. Abstr.*, pp. 06593, Vienna, 2005.
- Johnson, B. J., Oltmans, S. J., Vomel, H., Smit, H. G. J., Deshler, T., and Kroger, C.: Electrochemical concentration cell

- (ECC) ozonesonde pump efficiency measurements and tests on the sensitivity to ozone of buffered and unbuffered ECC sensor cathode solutions, *J. Geophys. Res.*, 107(D19), 4393, doi:10.1029/2001JD000557, 2002.
- King, J. C. and Turner, J.: Antarctic meteorology and climate, Cambridge University Press, UK, ISBN 0-521-46560-5, 1997.
- Kohmyr, W. D.: Electrochemical concentration cells for gas analysis, *Ann. Geophys.*, 25, 203–210, 1969, <http://www.ann-geophys.net/25/203/1969/>.
- König-Langlo, G., King, J. C., and Pettre, P.: Climatology of three coastal Antarctic stations Dumont d'Urville, Neumayer, and Halley, *J. Geophys. Res.*, 103, 10 935–10 946, 1998.
- Kreher, K., Johnston, P. V., Wood, S. W., Nardi, B., and Platt, U.: Ground-based Measurement of tropospheric and stratospheric BrO at Arrival Heights, Antarctica, *Geophys. Res. Lett.*, 24, 3021–3024, 1997.
- Langenberg, S. and Schurath, U.: Ozone destruction on ice, *Geophys. Res. Lett.*, 26, 1695–1698, 1999.
- Leser, H., Hönninger, G., and Platt, U.: MAX-DOAS measurements of BrO and NO₂ in the marine boundary layer, *Geophys. Res. Lett.*, 30(10), 1537, doi:10.1029/2002GL015811, 2003.
- MacDowall, J.: Some observations at Halley Bay in seismology, glaciology and meteorology, *Proc. Royal Soc. Lond. A.*, 256, 149–192, 1960.
- McConnell, J. C., Henderson, G. S., Barrie, L., Bottenhheim, J., Niki, H., Langford, C. H., and Templeton, E. M. J.: Photochemical bromine production implicated in Arctic boundary-layer ozone depletion, *Nature*, 355, 150–152, 1992.
- Oum, K. W., Lakin, M. J., and Finlayson-Pitts, B. J.: Bromine activation in the troposphere by the dark reaction of O₃ with seawater ice, *Geophys. Res. Lett.*, 25, 3923–3926, 1998.
- Peterson, M. C. and Honrath, R. E.: Observations of rapid photochemical destruction of ozone in snowpack interstitial air, *Geophys. Res. Lett.*, 28, 511–514, 2001.
- Platt, U. and Lehrer, E.: Arctic tropospheric ozone chemistry, Air pollution research report No. 64, edited by: Platt, U. and Lehrer, E., ISBN 92-828-2350-4, A89–A98, 1997.
- Rankin, A. M., Wolff, E. W., and Martin, S.: Frost flowers: Implications for tropospheric chemistry and ice core interpretation, *J. Geophys. Res.*, 107(D23), 4683, doi:10.1029/2002JD002492, 2002.
- Richter, A., Wittrock, F., Eisinger, M., and Burrows, J. P.: GOME observations of tropospheric BrO in northern hemisphere spring and summer 1997, *Geophys. Res. Lett.*, 25, 2683–2686, 1998.
- Roscoe, H. K., Kreher, K., and Friess, U.: Ozone loss episodes in the free Antarctic troposphere, suggesting a possible climate feedback, *Geophys. Res. Lett.*, 28, 2911–2914, 2001.
- Tang, T. and McConnell, J. C.: Autocatalytic release of bromine from Arctic snowpack during polar sunrise, *Geophys. Res. Lett.*, 23, 2633–2636, 1996.
- Vogt, R., Crutzen, P., and Sander, R.: A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, *Nature*, 383, 327–330, 1996.
- WDCGG (World Data Center for Greenhouse Gases)/AWI: Surface O₃ daily values, <http://gaw.kishou.go.jp/wdcgg.html>, WMO/WDCGG, JMI, 2003.
- Wagenbach, D., Ducroz, F., Mulvaney, R., Keck, L., Minikin, A., Legrand, M., Hall, J. S., and Wolff, E. W.: Sea-salt aerosol in coastal Antarctic regions, *J. Geophys. Res.*, 103, 10 961–10 974, 1998.
- Wessel, S., Aoki, S., Winkler, P., Weller, R., Herber, A., Gernandt, H., and Schrems, O.: Tropospheric ozone depletion in Polar regions A comparison of observations in the Arctic and Antarctic, *Tellus* 50B, 34–50, 1998.